

California Regional Water Quality Control Board  
North Coast Region

Laguna de Santa Rosa TMDL

Quality Assurance Project Plan

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## Table of Contents

1.0	INTRODUCTION, PURPOSE, AND RESPONSIBILITIES .....	4
1.1	Watershed-Specific Monitoring Plans .....	5
1.2	Implementation of QAPP.....	6
2.0	FIELD SAMPLING PROCEDURES.....	7
2.1	Collecting Water Samples.....	7
2.1.1	<i>Clean Sampling Technique</i> .....	7
2.2	Sample Preparation .....	8
2.2.1	<i>Bottle Inventory</i> .....	8
2.2.2	<i>Container Type &amp; Volume</i> .....	8
2.3	Transport of Water Quality Samples to the Analytical Laboratory .....	9
2.4	Sample Custody .....	9
2.5	Field Instrument Measurements.....	9
2.5.1	<i>Continuous Dataloggers – Temperature</i> .....	10
2.7	Equipment Needs .....	10
3.0	QUALITY CONTROL PROCEDURES.....	11
3.1	QC Samples .....	11
3.2	Analytical Laboratory QA .....	11
3.3	Data Acceptance Criteria .....	12
3.3.1	<i>Laboratory</i> .....	12
3.3.2	<i>Field Measurements</i> .....	12
4.0	DATA QUALITY OBJECTIVES .....	14
4.1	Data Usage .....	14
4.2	Relevant Environmental Indicators.....	15
4.2.1	<i>Temperature</i> .....	15
4.2.2	<i>Dissolved Oxygen</i> .....	15
4.2.3	<i>pH</i> .....	16
4.2.4	<i>Nutrients</i> .....	16
4.2.5	<i>Chlorophyll and Pheophytin</i> .....	16
4.2.5	<i>Total Suspended Solids</i> .....	16
4.2.5	<i>Mercury</i> .....	16
4.3	Specific Data Quality Objectives for the Laguna Watershed TMDLs .....	16
4.4.	Data Quality Indicators .....	18
4.4.1	<i>Precision</i> .....	18
4.4.2	<i>Accuracy</i> .....	19
4.4.3.	<i>Completeness</i> .....	19
4.4.4.	<i>Contamination</i> .....	19
4.5	Representativeness.....	20
4.5.1	<i>Selection of Sampling Sites and Locations</i> .....	20
4.5.3	<i>Sample Size</i> .....	21
4.6	Comparability .....	21

5.0 DATA ASSESSMENT .....	22
5.1 Data Review .....	22
5.2 Data Validation .....	23
5.3 Reanalysis (Rerun) Request .....	23
6.0 COMPILATION AND USE OF SECONDARY DATA .....	24
7.0 DOCUMENTATION AND RECORDS .....	26
7.1 Documentation .....	26
7.1.1 <i>Field Records</i> .....	26
7.1.2 <i>Corrections to Documentation</i> .....	27
8.0 REFERENCES CITED .....	28
9.0 ACRONYMS .....	29

## **1.0 INTRODUCTION, PURPOSE, AND RESPONSIBILITIES**

The objective of monitoring in support of Total Maximum Daily Loads (TMDLs) in the Laguna de Santa Rosa watershed (Laguna Watershed) is to produce data that represent, as closely as possible, the existing and to some extent historical environmental conditions of the waters in the basin. One way to ensure that this objective is met is by conducting monitoring in accordance with a Quality Assurance Project Plan (QAPP).

Some degree of error is inevitable in making measurements of any type. If not understood and minimized, these errors can lead to unacceptable uncertainty in the decision-making process. The purpose of this Laguna Watershed TMDL QAPP is to improve the quality of environmental data that is used for making decisions regarding TMDLs and water quality management for the Laguna Watershed.

The Laguna Watershed TMDLs QAPP presents guidelines for:

- Field sampling procedures;
- Quality control procedures;
- Data quality objectives;
- Data assessment;
- Use of secondary data; and
- Documentation.

Quality Assurance (QA) includes the overall management system of a project including planning, data gathering, quality control, documentation, evaluation, and reporting. QA will help to set the level of data quality needed and will help to determine whether the data meet the project's objectives.

Quality Control (QC) includes the set of activities intended to control errors and to meet the QA objectives.

Measurement Quality Objectives (MQOs) are acceptance criteria for the quality attributes measured by project data quality indicators. They are quantitative measures of performance (USEPA, 2002). MQOs are the targets for precision, bias and sensitivity against which laboratory QC results are compared. Precision is assessed from the results of replicate analyses of samples and standards. Bias is assessed from method blanks, check standards and matrix spikes to their expected values. Sensitivity is related to the detection and reporting limits for the measurement method used.

Some data collected for the TMDL are based on field measurements (i.e., stream flow). While there is no reference standard for these types of data, some components of bias and precision in the measurements can be evaluated and controlled as described elsewhere in this document.

Data Quality Objectives (DQOs) are used where the results are compared to a standard or used to select between two alternative conditions.

Data collected under this QAPP used for the following purposes:

- Background and data analysis for the TMDL staff report.
- Water quality modeling needed to establish TMDLs.

This QAPP incorporates guidance from the QAPP prepared for the Surface Water Ambient Monitoring Program (SWAMP) developed by the California State Water Resources Control Board (2002). The SWAMP QAPP was developed for ambient surface water monitoring, and is useful for guiding TMDL monitoring efforts in the Laguna Watershed.

## **1.1 Watershed-Specific Monitoring Plans**

The watershed-specific monitoring plan that will be used in conjunction with this QAPP has been developed for the Laguna Watershed. The watershed-specific monitoring plan is a written plan that specifies the objectives, rationale, and procedures for collecting and analyzing samples or physical environmental attributes of interest to TMDL development. The plan describes the sampling needed to achieve the stated objectives (i.e., the variables to be measured, the number and locations of sites to be sampled, and the number and frequency of sampling events).

Watershed-specific monitoring plans for the Laguna Watershed TMDLs provide data that will serve several purposes, including:

- Hypotheses and a statement of sampling purpose.
- Provides preliminary survey or screening information about surface waters.
- Characterizes existing water quality conditions and possible beneficial use impairments.
- Assesses historical water quality conditions and beneficial use impairments.
- Identifies spatial and temporal variation or trends in water quality over time
- Provides specific data for water quality models used to develop TMDLs
- Identifies specific existing or emerging water quality problems
- Assists in developing a TMDL implementation plan.

Sampling may answer questions such as:

- Are beneficial uses impaired?
- What are the current levels of impairments?
- How does water quality vary temporally and spatially?
- Which water quality constituents or physical environmental attributes are the best indicator variables for describing the impairments?
- How does the timing and spacing of the most sensitive beneficial use overlap with water quality constituents?
- What relative impacts to impairment from specified human-caused sources vs. natural sources?
- What are the watershed loading capacities of pollutants impairing beneficial uses?
- How should pollutant loads be allocated among natural sources, human-caused sources, with a margin of safety to account for uncertainties?

## 1.2 Implementation of QAPP

The primary QA responsibilities fall on the individual TMDL watershed project managers. These personnel will develop watershed-specific monitoring plans, establish project-specific DQOs, and review laboratory and field QA data to ensure that DQOs are met. The TMDL Development Unit Senior shall serve a QA function by ensuring that watershed-specific plans and DQOs are appropriate, and approving watershed-specific monitoring plans, including changes from the overall Laguna Watershed QAPP. The TMDL Development Unit Senior will validate 10% of field and laboratory QA data to ensure that standards are met, and will perform (or arrange for) evaluation field visits to ensure that the field sampling crew are using appropriate procedures, consistent with the QAPP. The following table shows the QA roles and responsibilities for North Coast Regional Water quality Control Board (NCRWQCB) TMDL monitoring plans.

<b>QA Roles &amp; Responsibilities in the Laguna Watershed TMDLs</b>	
<b>Role</b>	<b>QA Responsibility</b>
TMDL Unit Senior	<ul style="list-style-type: none"> <li>• Review and approve TMDL-related QAPPs and DQOs</li> <li>• Review proposed TMDL sampling/monitoring plans to ensure that QA objectives will be met</li> <li>• Validate at least 10% of the TMDL-related QA data</li> <li>• Conduct performance audits, as appropriate</li> </ul>
TMDL Watershed Project Manager	<ul style="list-style-type: none"> <li>• Develop TMDL project-specific DQOs</li> <li>• Modify the overall Laguna Watershed QAPP, as needed, for a specific project</li> <li>• Design appropriate monitoring and data gathering plans</li> <li>• Document the changes and rationale for changes to the overall Laguna Watershed QAPP</li> <li>• Verify that the QAPP is implemented</li> <li>• Review and assess laboratory and field QA results for DQO compliance</li> <li>• Interpret and apply results from monitoring plans</li> <li>• Retain data for further review</li> <li>• Maintain records and documents</li> <li>• Communicate with the analytical laboratory to ensure QA and QC are met</li> </ul>
Field Monitoring Crew	<ul style="list-style-type: none"> <li>• Assure that the QAPP is implemented in field activities</li> <li>• Follow proper field procedures, as described in the field sampling plan, including field documentation and sample handling</li> <li>• Document changes and rationale for field changes to the monitoring plans</li> <li>• Maintain custody of samples</li> <li>• Ensure delivery of samples to laboratory</li> </ul>

## **2.0 FIELD SAMPLING PROCEDURES**

### **2.1 Collecting Water Samples**

Water samples can be collected as single grab samples collected just below the surface in the center of the stream. When collection from the center of flow is not safe or possible, collection will be made from a safely accessible well-mixed area. Care should be taken to ensure that sediment is not disturbed when taking a water column sample. Avoid surface debris when collecting water samples. Field replicate samples will be collected in rapid succession as the regular sample. The field monitoring crew will describe where samples were obtained, including a site description. If an alternate site is chosen the samplers will fully describe in field notes the location and the reason for the change.

Water samples will be collected in the appropriate containers and preserved as directed by the analytical laboratory. Physical preservation includes cooling and keeping samples out of sunlight. Samples will be labeled and placed on ice in an ice chest immediately after collection. Field replicate samples and field blank samples will be handled and processed as regular samples. Chlorophyll and pheophytin samples will be placed on ice and filtered as soon as possible. Labels on each collection bottle will note:

- Project number or name
- Sampling location
- Time and date sampled
- Analysis type (parameter)
- Sample matrix (water, sediment or filter)
- Preservative used
- Initials of collectors

#### ***2.1.1 Clean Sampling Technique***

If data quality requirements for a specific sampling event require the use of very high quality data or very low detection limits, the use of U.S. Environmental Protection Agency (EPA) “clean sampling” technique may be required. This technique may be especially useful for detecting low levels of mercury. See the SWAMP QAPP for specific directions on employing these techniques. In brief the steps for the technique are:

- Samples are collected using rigorously pre-cleaned sample bottles that are double bagged to prevent contamination
- The sample labels are placed on the outside of the outer bag to avoid contamination
- At least two persons are required, each wearing a double set of clean poly gloves
- The person designated “dirty hands” touches and opens only the outer bag of all double-bagged items, avoiding touching the inner bag
- The person designated “clean hands” reaches into the outer bag, opens the inner bag and removes the clean sample bottle
- “Clean hands” closes the inner bag and “dirty hands” closes the outer bag

- “Clean hands” removes the sample bottle lid under water and holds it underwater while performing the required number of rinses with ambient water
- “Clean hands” collects the sample and places the lid on the bottle while holding the bottle and cap under water
- The water sample is re-bagged in the opposite order from which it was removed
- Gloves must be changed whenever something known to not be clean is touched

## 2.2 Sample Preparation

### 2.2.1 Bottle Inventory

The field monitoring team will inventory bottle sets upon receipt from the laboratory to ensure that the proper type of bottles and an adequate number of bottles have been received for the planned sampling event. All bottles will be labeled before the sampling event, except for the time and date of sampling. Apply labels to the bottle and not to the cap. In the field, fill in the time and date of sampling and tape over the label to ensure that the label adheres even when wet.

### 2.2.2 Container Type & Volume

The analytical laboratory will provide containers appropriate for the target analytes. The analytical laboratory also will recommend required typical sample volumes, which may be less than that shown below if samples for several analytes are combined in one container. Unless directed otherwise by the laboratory, the following guide can be used. The analytes listed in the table below are those planned to be sampled for in the Laguna Watershed TMDL.

Sampling Guide					
Analyte	Method	Container	Preservative	Hold (days)	Volume Needed
Total Mercury	EPA 7000 Series	Poly	HNO <sub>3</sub> to pH<2	28	250 ml
Total Suspended Solids	EPA 160.2	Glass or Plastic	Store cool at 4°C	7	250 ml
Ammonia-N	EPA 350.3	Poly	H <sub>2</sub> SO <sub>4</sub> to pH<2; Store cool at 4°C	28	250 ml
Total Kjeldahl-N	EPA 351.2	Glass or Plastic	H <sub>2</sub> SO <sub>4</sub> to pH<2; Store cool at 4°C	28	250 ml
Nitrate-N	EPA 353.2	Poly	Store cool at 4°C	2	50 ml
Ortho-Phosphate	EPA 365.2	Poly	Store cool at 4°C	2	50 ml
Total Phosphorus	EPA 365.2	Poly	H <sub>2</sub> SO <sub>4</sub> to pH<2 Store cool at 4°C	28	50 ml
Biochemical Oxygen Demand	EPA 405.1 SM 5210A/B	Poly	Store cool at 4°C	2	
Chlorophyll Pheophytin	SM 10200H	Filter in Field	Store on Dry Ice	30	amt. varies

### **2.3 Transport of Water Quality Samples to the Analytical Laboratory**

Transport of samples to the analytical laboratories will be done by overnight courier (such as Federal Express) in sealed coolers with ice and the appropriate chain-of-custody forms. Samples will be maintained on ice. Spouts on coolers should be sealed before shipping. Not all analytes require refrigeration or darkness, but, for the sake of simplicity it is suggested that all be stored dark on ice in closed coolers. Sample collection schedules must be coordinated with the analytical laboratory. Sample transport scheduling will ensure that the laboratories receive samples in time to process the samples without exceeding the appropriate holding times. Sample holding times and conditions will be confirmed with the analytical laboratory.

### **2.4 Sample Custody**

Maintaining custody of the water quality samples (i.e., being able to show an unbroken trail of accountability that ensures the physical security of sample) is important for ensuring the credibility of the data derived from the sample. A sample is considered to be “in custody” if it:

- Is in actual possession;
- Is in view after being in physical possession; or,
- Is placed in a secure area accessible only to authorized persons.

Chain-of-custody (COC) forms are used to document the custody and transfer of samples from the time they are collected to the time that they are analyzed. Completed COC forms also are used as a reference to correlate the field sample identification numbers with the internal laboratory sample identification numbers.

The analytical laboratory will provide COC forms to be used in this project. Information needed on the COC forms includes: project name, required laboratory turnaround time, sample identification number, date and time sampled, matrix description, number of containers for each sample identification number, container type, analyses requested, type of preservation (e.g., acid, ice) and signatures of responsible parties when custody is received or released.

Field personnel who collect samples will initiate the COC while in the field. COC forms will be completed at each sample location and will accompany the transported samples to the analytical laboratories. A copy of the COC form will be retained before shipping. If the field crew delivers the samples to the laboratory, copies of the released chain-of-custody forms will be retained. The laboratory will sign the COC form upon receiving custody of the samples. The laboratory will return a copy of the completed COC form with the report of analytical results.

### **2.5 Field Instrument Measurements**

Water quality data from the field instruments will be collected at the same location as the water samples. The field measurements will be collected in a manner that will not disturb the water samples (i.e., by obtaining measurements after the water samples have been collected or by using the field instruments just downstream of the sample collection point). The TMDL watershed manager will select the field sampling protocols that best suit the specific DQOs

adopted for sampling in that watershed. Specific instructions for the use of each instrument will be available to the field monitoring team.

The following parameters will be analyzed from the field instruments:

- Water temperature
- Dissolved oxygen (DO)
- Specific conductance
- pH
- Water velocity at sampling location and depth

The NCRWQCB uses Yellow Springs Instrument (YSI) Datasonde dataloggers for instantaneous measurement of pH, dissolved oxygen, temperature, and conductivity and the YSI SonTek Acoustic Doppler Velocimeter (ADV) for flow measurement. The manufacturer's manuals will be used for guidance on equipment use, calibration, and maintenance. Before deploying continuous instruments, ensure that the internal time and date of each instrument is calibrated, using a calibrated clock. The battery life on each instrument should be checked to ensure that the instrument will be able to collect data over the entire time period desired.

### ***2.5.1 Continuous Dataloggers – Temperature***

Optic Stowaway data loggers are used by the NCRWQCB for unattended, continuous temperature monitoring. The Optic Stowaways will be set to record water temperature at intervals as directed by the monitoring plan. Optic Stowaways will be located as directed by the monitoring plan, but actual placement will depend on finding a location that is in a well-mixed flowing area that is concealed from the casual observer. The Optic Stowaway data loggers can be zip-tied to trees on the bank or to stakes driven into the bank. Measurements from a notable landmark, such as a large rock, to the bank stake or cabled tree will be made and noted. Since the water levels in the Laguna Watershed may begin to dry up in late summer, the Optic Stowaways should be located so that they remain in the water. The instruments should be checked and redeployed, if necessary, at regular intervals. All temperature loggers will be calibrated in room temperature and ice water before and after the sampling season.

## **2.7 Equipment Needs**

The SWAMP QAPP has a list of equipment commonly needed for water quality sampling. Additional equipment for measuring other environmental indicators may be required for the Laguna Watershed TMDL monitoring. Care should be taken to ensure that the equipment, supplies, or methods used do not interfere with the analytes of interest. The TMDL field sampling crew will ensure that all necessary equipment and supplies are taken on sampling trips. The following equipment/supply checklist may be used.

### **3.0 QUALITY CONTROL PROCEDURES**

#### **3.1 QC Samples**

Water quality QC samples will consist of field replicates and field blanks. The QC samples will be rotated randomly among the sites and among analytes. All field replicate samples and field blanks will be submitted to the analytical laboratory blind. In other words, a fictitious site name will be given for these field QC samples.

Field replicate samples consist of three samples collected from the same source. Field replicates will consist of three grab samples collected in immediate, rapid succession. Field duplicates will be collected at a rate of 10% of all analyses for a particular analyte. Field blanks will be used to assess possible contamination that can occur during field sampling and handling. In the field, fill a sample container with distilled water and subject this blank to the same handling and processing as other samples. The SWAMP QAPP recommends using field blanks for the initial samples – further use of field blanks is not required if the initial field blanks are within specification. This QAPP will adopt the SWAMP QAPP recommendations regarding the frequency of field blanks.

TMDL watershed managers may select a different number of required QC samples (field duplicates and blanks), based on calculations of the numbers of samples necessary to achieve a given probability of detecting a specified level of certainty. These calculations require information about the specific watershed and will involve either screening sampling or the use of historic data to evaluate expected variability in the samples.

#### **3.2 Analytical Laboratory QA**

Specific quality control procedures for analytical laboratories are not included in this QAPP because each contract laboratory has internal QA/QC operating procedures and protocols available for review. If there are questions about the results from a specific laboratory, the TMDL watershed project manager should ask to review the procedures with the lab's contract manager and QA officer.

The analytical laboratory should report a complete data package to the TMDL manager. At a minimum, the laboratory report should include:

- Results of sample analyses
- sample ID numbers
- sample matrix type
- date of sample receipt
- date of extraction
- analyte name
- tabulated analytical results
- laboratory qualifier flags with notes of explanation

- reporting limits for each analyte
- Dilution
- Methods
- Results of replicate samples (result, reporting limit)
- Results of method/laboratory blanks (result, reporting limit)
- Results of matrix spikes (result, reporting limit, spike level, % recovery)

### **3.3 Data Acceptance Criteria**

Data acceptance criteria are pre-established criteria used to determine whether data fall within the limits of acceptability for QA purposes. When the data do not meet the acceptance criteria they should be marked to ensure that the associated problem is identified. Often, the data still may be useful for its intended purpose.

#### **3.3.1 Laboratory**

The analytical laboratory shall include QA data with the analytical results. Items identified by the laboratory as problematic should be flagged. The TMDL manager should discuss the flagged items with the analytical laboratory to determine if the sample should be reanalyzed or to determine the effect of the problem. Examples of data that might be flagged for further investigation are:

- Results with a high reporting limit
- Results from samples received outside of the recommended holding times
- Results with matrix interference requiring dilution
- Spike recoveries outside control limits
- Results from blind duplicates not in close agreement
- Duplicate results with a high relative percent difference.

#### **3.3.2 Field Measurements**

Water quality field instruments will be calibrated at the beginning and end of the sampling event. Field instruments will be calibrated as described in the owner's manuals for the individual instruments. As directed by the SWAMP QAPP, field instruments will be calibrated within 24 hours before use and within 24 hours after field use. Calibration records are to be maintained in a logbook for each instrument or in field record sheets. These records are to be reviewed by the TMDL watershed project manager before the data generated from the field measurements can be reported in a TMDL document.

As part of the calibration process, the TMDL watershed project manager will check instrument calibration constants against the acceptable range published by the manufacturer or by the SWAMP QAPP. For the YSI Datasonde these constants include conductivity cell constant, pH millivolt, pH slope, DO charge, and DO gain. For the SonTek ADV these constants include Signal to Noise Ratio, probe angle, and standard error of velocity. Out-of-specification or out-

of-range calibration results will not be accepted. Never over-ride a calibration error message in the field without understanding the cause.

The SWAMP QAPP guidance states that post-run calibration data that have drifted beyond acceptable limits should be flagged and, in most cases, the data collected should be rejected. The SWAMP QAPP encourages the field monitoring team to repeat the field measurements as soon as possible if data are rejected. A field record sheet used by the SWAMP program for daily field instrument calibration can be found in the SWAMP QAPP Manual.

As mentioned, field instruments will be calibrated according to the specifications in the owner's manual for the individual instruments. Specific instructions for field calibration of each instrument will be available to the field monitoring team. The following itemizes specific considerations for calibration procedures:

- Altitude, barometric pressure and temperature influence calibration, therefore, it is desirable to calibrate instruments onsite, using standard calibration solutions that are at ambient river temperature.
- Calibration of conductivity will be done before pH calibration to avoid interference by pH standards that have high conductivity.
- Specific conductivity will be calibrated using standard potassium chloride calibration solution.
- Instruments used to measure pH will be calibrated using standard pH buffers. Two-point pH calibration is usually acceptable for the Laguna Watershed TMDL fieldwork. Use two pH values that will bracket the expected values (usually pH calibration standards of 7.00 and 10.00 are used). If the pH range of the water under investigation is unknown, use a three-point pH calibration.
- Temperature, measured by a multi-parameter instrument such as a YSI 6600, is factory set and does not require calibration.
- Temperature, as measured by continuous, unattended devices such as Optic Stowaways, will be calibrated in two temperature baths (room temperature and ice water) with an NIST-traceable thermometer.
- Dissolved oxygen, measured by a multi-parameter instrument such as a YSI 6600, will be calibrated using water-saturated air, accounting for elevation, barometric pressure and temperature.

## **4.0 DATA QUALITY OBJECTIVES**

Data quality objectives (DQOs) are project-specific qualitative or quantitative statements of the overall level of confidence that is needed for decision-making or data interpretation. DQOs define the total uncertainty that can be tolerated in a project dependent on data collection. Assessing whether the purpose of the QAPP is accomplished (e.g., whether, and to what degree, the data collected represent the true environmental conditions in the basin) will be accomplished by establishing DQOs for laboratory and field measurements in terms of detection levels, precision, accuracy, completeness, comparability and representativeness. DQOs are derived before an investigation begins by establishing criteria that:

- Clarify the study objective
- Define the most appropriate type of data to collect
- Define the number of samples or observations that must be obtained in order to have an acceptably robust set of data
- Determine the most appropriate conditions under which data should be collected
- Specify tolerable limits on errors.

Well-designed DQOs, in effect, support the level of data quality needed. Data quality can be quantified by the parameters of precision, accuracy, representativeness, completeness, and comparability, which determine the appropriate sample collection and analyte identification and detection methods to employ. Consider the consequences of error – stringent performance parameters are required in applications where severe consequences may result from a decision based on inaccurate data, whereas other applications may require less stringent performance parameters.

The use of appropriate project-specific DQOs can minimize costs associated with being overly stringent in making observations or taking samples, while, at the same time allowing collection of data of sufficient quality and quantity to support defensible decision-making. DQOs will be balanced against the time and available resources. Less rigorous DQOs may be established if the project manager can justify the standards with specific statements explaining the chosen DQO levels or elements.

### **4.1 Data Usage**

The purposes for which data will be used help to define the appropriate data quality objectives for a project. The data gathered in the Laguna Watershed TMDL effort will be used in characterizing aquatic systems, developing waste load allocations and loading capacities, and in ascertaining whether the pollutants are derived from natural or human-caused sources. The data generally will be applied to understand conditions at a watershed scale. Data that are considered critical for the TMDL project decision-making may undergo closer scrutiny than data that are needed for informational or background purposes.

## **4.2 Relevant Environmental Indicators**

In developing watershed-specific monitoring plans for the Laguna Watershed TMDLs the data collection should focus on indicator variables that are:

- Quantitatively related to the beneficial use that is impaired
- Sensitive to land use activities or stresses
- Reliably measurable.

The following water quality indicators are included in the Laguna Watershed TMDL monitoring program:

- Instantaneous general field parameters (water temperature, pH, dissolved oxygen, conductivity)
- Continuously monitored parameters (water temperature, air temperature)
- Biochemical oxygen demand (BOD)
- Nutrient species
- Chlorophyll and pheophytin
- Total suspended solids
- Mercury

Additionally, the measurements of the following physical environmental attributes are included:

- Air temperature and relative humidity
- Flow
- Channel characteristics
- Riparian characteristics

These parameters are considered valid indicators for assessing water quality in the Laguna Watershed TMDLs field sampling effort for the reasons discussed below.

### ***4.2.1 Temperature***

Water and air temperature measurements are necessary because surface water in the Laguna Watershed is listed on the California Section 303(d) list for high temperature. Water temperature data collected by continuous monitors at 30-minute increments is used for system description; model calibration, model validation, model application; and, identification of critical thermal maximums and persistence of maximums. Understanding the timing and persistence of high water temperatures is needed to understand the potential impacts to beneficial uses. Air temperature is related to water temperature and will be measured at select sites for characterizing microclimatic conditions.

### ***4.2.2 Dissolved Oxygen***

Understanding the timing and persistence of low dissolved oxygen or pH extremes is needed to assess the potential impacts to beneficial uses. The concentration of dissolved oxygen and pH levels in water are directly related to aquatic life beneficial uses. Dissolved oxygen

measurements are necessary because surface waters in the Laguna Watershed are listed on the California Section 303(d) list for low DO. Dissolved oxygen will also be measured in order to provide input to water quality models. The dissolved oxygen measurements can be used to identify critical DO minima and persistence of these minima. BOD is also being measured to understand the source of low dissolved oxygen.

#### **4.2.3 pH**

pH data will assist in understanding toxicity potential for ammonia. pH also can be an indicator of biological activity. There may be a diel pH cycle – water column pH can increase in late afternoon due to the removal of carbon dioxide by photosynthesis and it may decrease in the early morning due to overnight respiration.

#### **4.2.4 Nutrients**

Measurement of nutrient species (nitrate, ammonia, total Kjeldahl nitrogen, total phosphorus, and ortho-phosphate) is planned because surface waters in the Laguna Watershed are listed on the California Section 303(d) list for nutrient enrichment. Nutrient enrichment may lead to direct impacts on aquatic life beneficial uses (e.g., ammonia toxicity) or to indirect effects, such as low dissolved oxygen caused by excess algal growth or by nitrification reactions.

#### **4.2.5 Chlorophyll and Pheophytin**

Chlorophyll is useful in evaluating nutrient enrichment and dissolved oxygen in an aquatic system. Chlorophyll and pheophytin can be used to assess the biological response of a surface water to nutrient enrichment. The Laguna Watershed is listed on the California Section 303(d) list for nutrient enrichment. Knowledge of chlorophyll levels is also for input to the water quality modeling efforts in the Laguna Watershed TMDL. Pheophytin measurements are of interest because chlorophyll and pheophytin together can indicate total living and dead algae in a sample and can help to explain the algal population dynamics.

#### **4.2.5 Total Suspended Solids**

Total suspended solids will be measured to evaluate the effects of land use on sedimentation in the Laguna Watershed. The Laguna Watershed is listed on the California Section 303(d) list for sedimentation. Total suspended solids have been directly related to potential adverse effects on aquatic life beneficial uses as well as filling of the Laguna with excess sediment.

#### **4.2.5 Mercury**

Mercury is analyzed to describe the quality of fish tissue of the Laguna Watershed. The Laguna Watershed is listed on the California Section 303(d) list for mercury contamination of game fish. This mercury contamination can impair human health.

### **4.3 Specific Data Quality Objectives for the Laguna Watershed TMDLs**

Specific QA DQOs for the Laguna Watershed TMDL monitoring are shown in Tables 4.1 and 4.2 below. A discussion of each data quality indicator (i.e. precision, accuracy, completeness, contamination, and representativeness) follows the tables.

**4.3.1 Analytical Samples**

<b>Table 4.1 Specific QA DQOs for the Laguna Watershed TMDLs Analytical Laboratory Samples</b>		
<b>Data Quality Indicator</b>	<b>Data Quality Measurement Technique</b>	<b>Acceptable Limits</b>
Precision	Relative Percent Difference	≤25% for water samples ≤35% for soil samples
Accuracy	Spike Recovery	80-120%
Completeness	% Valid Data	90% of total data
Contamination	Field Blank Concentrations	<10% of the lowest sample concentration reported in the associated sampling run or less than two times the reporting limit

**4.3.2 Field Measurements**

Data quality indicators for field water quality measurements (i.e. temperature, pH, and dissolved oxygen) and for other field measurements (such as stream flow) are more difficult to measure than those for laboratory samples. Recommended ways to measure data quality indicators when evaluating data from field instruments and field observations are shown in Table 4.2. Precision, accuracy, and completeness are more of a concern in field measurements than is contamination.

<b>Table 4.2 Specific QA DQOs for the Laguna Watershed TMDLs Field Measurements</b>		
<b>Data Quality Indicator</b>	<b>Data Quality Measurement Technique</b>	<b>Acceptable Limits</b>
Precision	Use the same instrument or method to make repeated analyses on the same sample	≤ 25% difference in repeated measurements
	Use the same instrument or method to make repeated measurements at the same site under identical conditions	
Accuracy	Comparison of same measurements using: <ul style="list-style-type: none"> <li>• different methods</li> <li>• different instruments</li> <li>• different operators</li> </ul>	80-120% agreement
	Take multiple measurements and use the median of the results	
	Equipment Calibration	See later discussion of acceptable calibration results
Completeness	% Valid Data	90% of total data

#### **4.4. Data Quality Indicators**

##### **4.4.1 Precision**

Precision describes how well repeated measurements agree, i.e., the reproducibility of the data. Precision is not related to the true value of the data. For analytical laboratory samples used in the Laguna Watershed TMDLs, precision will be measured as the coefficient of variation (CV). The coefficient of variation is presented as a percentage of the standard deviation divided by the mean of the 3 replicate samples collected.

If the CV is greater than 25% for water samples and the absolute difference is greater than the reporting limit, samples should be reanalyzed, if possible. If the CV remains greater than the objective after reanalysis or if reanalysis is not possible, then the results should be qualified as “estimated.” Use of the median value of the three replicates represents the best measure of central tendency since the data are likely to not follow a normal distribution.

For field measurements, precision may be measured in different ways:

- Use the same instrument or method to make repeated analyses on the same sample
- Use the same instrument or method to make repeated measurements at the same site under identical conditions

For field measurements, repeated values shall be within 25% of one another.

When the precision objectives are not met, the TMDL watershed project manager will attempt to determine the source of the sample variability. The SWAMP QAPP states that consistent

failure of samples to meet the precision objectives may be related to a lack of homogeneity in the sample, unusually high concentrations of the analytes, or poor laboratory precision.

#### **4.4.2 Accuracy**

Accuracy is a measure of how close the measured value is to its true value. Unless the true value of a sample is known, accuracy cannot be evaluated. The accuracy of results of analytical laboratory samples can be assessed by the percent recovery of a known reference spike added to a sample. This can be done in the laboratory after the sample is received or it can be done in the field. For purposes of this QAPP, accuracy will be assessed by the analytical laboratory and not by using field spikes, unless specifically required by individual watershed-specific monitoring plans. The accuracy goal for the Laguna Watershed TMDL QAPP water samples will be 80-120% recovery. This limit will not apply when a sample value exceeds the spike concentration by greater than five times.

For field measurements, assessing accuracy is more difficult, because the true value cannot be determined as easily as in laboratory samples. Depending on the field measurement or instrument, accuracy can be assessed by comparing the same measurements (same site, identical conditions) using different methods, different instruments, or different operators.

The same quantitative goal of 80-120% of agreement should be used. Another way to reduce variability and enhance accuracy in field measurements is to occasionally take multiple measurements and use the mean or upper confidence interval of the results. Additionally, equipment calibration will help to ensure accurate results.

#### **4.4.3 Completeness**

Completeness is the fraction of the planned data that must be successfully collected and validated to fulfill pre-determined statistical criteria for the project. The percent of completeness needed for each project is typically based on the amount of data that is needed in order to reach valid conclusions and a subjective determination of the relative importance of the monitoring element within the monitoring plan. This, in turn, determines the necessary sampling frequency. Data may be considered unusable due to factors such as holding-time violations, improper sample preservation, laboratory error, insufficient sample volume, loss of samples during shipping, or incorrect field technique. The completeness goal for the Laguna Watershed TMDL QAPP will be 90% (i.e., 90% of the data collected should be valid and useable).

#### **4.4.4 Contamination**

Field blanks (described in Section 3.1) can be used to assess sample contamination that can occur from equipment or during field sampling and handling. Blanks are samples that are supposed to be free of the analytes of interest. Field blanks are usually distilled water that is taken into the field, poured into the sample container, and subjected to the same handling and processing as other samples. Field blanks are used to detect contamination that occurs in field handling and are often used for assessing contamination.

Considering the analytes of interest in the Laguna Watershed TMDLs, field blanks will be used to assess contamination. Distilled water can be obtained from a commercial store. If there has been no contamination, the analytical laboratory will report the value of a field blank as below the reporting limit. There may be some slight contamination from the laboratory that is unrelated to the field procedures. If this is the case, the acceptable concentrations reported for a field blank should be less than 10% of the lowest sample concentration reported in the associated sampling run or less than two times the reporting limit.

## **4.5 Representativeness**

Representativeness describes how relevant the data are relative to environmental conditions. Surface waters are temporally and spatially heterogeneous. In the context of the Laguna Watershed TMDL, representativeness relates to the selection of sampling locations, the daily and seasonal timing of the sampling events, and the use of appropriate sampling techniques. Representativeness is addressed by the overall design of the watershed-specific monitoring plans, especially with respect to selecting appropriate locations, methods, times, and frequency of sampling, and by maintaining the integrity of the samples after collection.

### **4.5.1 Selection of Sampling Sites and Locations**

The selection of sampling sites should be explained in the Laguna TMDL monitoring plan. The selection of sampling sites is important if the data collected are to be considered as representative of the system or of a part of the system. The Laguna TMDL monitoring plan addresses how the sample sites were selected, and whether the selection of a site could make the sample atypical or non-representative. If so, the bias resulting from the site selection must be addressed. Some of the reasons to select a specific site include:

- The site is representative of a reach of interest
- The site sample location provides samples that are well-mixed
- The site is at the confluence of a tributary
- The site is upstream or downstream of an input whose impact must be described
- The site describes a reach that is uniquely important for important beneficial uses, such as fish habitat
- The site complements or supplements sites for which historic data exist
- Site access is safe
- Site access on private property is allowed.

### **4.5.2 Sample Timing**

Each analyte of interest should be evaluated to determine if sample timing (time of day, watershed events, and season) might impact the measurement or the interpretation of the result. This evaluation will assist in determining the timing and frequency of sampling. Sample timing, as related to each analyte, should be explicitly discussed in the watershed-specific monitoring

plan. Examples of timing considerations that are applicable to the Laguna Watershed TMDL include:

- Variations in flow conditions (e.g. seasonal and management variations), which might affect the seasonal timing of sampling events
- Periods that are critical for sensitive beneficial uses, such as fry emergency, spawning, and migration, might be of particular interest for sampling
- Sampling frequencies for DO and water temperature should address the most sensitive time periods to sample since these parameters fluctuate daily and seasonally
- Sampling for mercury in water should not be done during periods of abnormally high turbidity

#### **4.5.3 Sample Size**

Determining the proper sample size to adequately characterize the watershed is an important decision. Too small or too large a sample size may lead to wasted resources. In general, as sample sizes increase the error associated with uncertainty decreases. A large number of measurements can increase precision, reduce the likelihood of bias, and increase the power of the statistical analysis of data.

#### **4.6 Comparability**

Comparability is the portion or fraction of planned data that can be compared directly to similar studies. There have been numerous previous water quality and environmental studies in the Laguna Watershed. In order to directly compare the planned data collection efforts to earlier efforts, comparable protocols, locations, timing, and instruments should have been used. If the sampling parameters were different, the project manager will have to review and evaluate the effects of the differences for impact on use in direct comparisons. Comparability also can be addressed by comparison of the analysis of standard reference materials used in the different sampling events.

## **5.0 DATA ASSESSMENT**

After each sampling event, QA data will be examined for compliance with the DQOs. If DQOs were not met, data should not be used in the TMDL analysis unless it can be demonstrated that there is not significant impact to the acceptability and usability of the data. If the data are considered useable, limitations on the data will be noted in the reports that rely on the data for decision-making.

If DQOs are not met, the QA procedures will be examined and corrective action will be implemented, if needed. Depending on the cause of the QA failure, corrective actions might include:

- Identifying contamination source, if possible
- Retraining the field sampling crew
- Re-calibrating field instruments and reanalyze
- Reanalyzing laboratory samples
- Changing the field instrument maintenance procedures
- Changing the sample handing or transport procedures
- Working with the laboratory QA manager to address laboratory QA issues
- Revising the QAPP
- Rescheduling sample events, if appropriate, to achieve more completeness

### **5.1 Data Review**

Data review will be performed routinely, in a timely manner, to ensure that all data have been logged and processed correctly. This includes checking data entry, transcription, calculations, data reduction, and data transfer. The process includes making sure that all pertinent data are included in the documentation and that there are no data deficiencies.

All results from the analytical laboratory should be critically reviewed as soon as possible with respect to precision, accuracy, completeness, and contamination DQOs. Further, laboratory results and other pertinent data should be examined for the following:

- Holding time review – check for prescribed holding times being exceeded
- Blank review – review blank analyses for evidence of potential contamination
- Matrix spike review – review matrix spike recovery ranges and matrix spike duplicate relative percent differences as a check for analytical accuracy and for extraction precision
- Elevated detection limits – identify samples with elevated detection limits as a result of sample dilution or small sample volume
- Replicate review – review replicate analyses for agreement of results as a check for analytical precision

Other reviews that are specific to the analyses requested should also be performed. For example, when reviewing nutrient data it is helpful to compare the concentrations of ortho-phosphate to total phosphorus. Other items to review include results when there was an unexpectedly high or low concentration of analytes. Sometimes data with questionable QA results can be used for their intended purposes, but the significance of the discrepancy must be understood, explained, and documented.

All results that are flagged by the laboratory will be reviewed and QA discrepancies investigated. Discussions with laboratory personnel may help to resolve questions about the analytical data. Corrective actions will depend on the type of discrepancy.

## **5.2 Data Validation**

The TMDL Development Unit Senior will validate at least 10% of TMDL development QA data. Validation is a determination about the quality of the data specific to its usability for decision-making and an evaluation of whether the watershed-specific QA requirements were met. This task reconciles the project objectives with the QA needs of the specific project and with the data that were used.

## **5.3 Reanalysis (Rerun) Request**

After review of the analytical or laboratory QA results the TMDL project manager may request that the analytical laboratory reanalyze a sample for a specific constituent or set of constituents. Usually, this is done if the laboratory QA results or field QA samples are outside of acceptable limits. A rerun also may be requested if the results fall outside of expected ranges or are otherwise atypical. Some atypical or out-of-specification results can be acceptably explained and do not require reanalysis, such as:

- Environmental or operational situations may provide an explanation for an atypical result.
- The samples may have been improperly preserved or handled. If so, reanalysis would not be expected to improve the representativeness of the samples.
- The sample locations may have been improperly recorded on the COC delivered to the laboratory.
- Samples may have been held past acceptable hold times.

If the reanalysis of a sample does not resolve the questions about the sample results, the TMDL watershed project manager should consider other approaches, including collecting new samples using different methods. Agreement of the results with the earlier questioned result indicates that the original value was probably correct. Disagreement between the original questioned result and the new sample result requires explanation and, most likely, a third sample to confirm either the original or the new sample result.

## **6.0 COMPILATION AND USE OF SECONDARY DATA**

There is a long history of data collection in the Laguna Watershed. These data and information are found in publicly available databases, data from other monitoring programs, results from unpublished research (including local watershed groups), academic thesis research, maps, literature, anecdotal information, models and model outputs, agency reports, census data, meteorological data, and other sources. For purposes of this Laguna Watershed QAPP, these types of data are known as historic or secondary data.

When secondary data are used in TMDL development, especially for purposes other than those for which the data were collected, the data quality and uncertainty of the data must be ascertained. Different types of data collected for different purposes may have QA that is not appropriate for the TMDL decision-making, even if the data are from a well-respected source. The TMDL watershed manager must ensure that the secondary data are not proprietary or otherwise subject to confidentiality.

In order to determine whether the secondary data have quality constraints that would limit their use in a new setting, it first must be understood how the data will be used in the TMDL decision-making process. Secondary data or information may be used, for example:

- As a screening tool to develop a new data gathering effort
- To provide qualitative weight of evidence to the results of new data collection
- To verify the results of new data
- To directly contribute to base data
- To substitute for some or all of a new data collection effort.

Depending on the intended use of the data in TMDL development, the TMDL watershed project manager must evaluate the secondary data and information for QA concerns pertinent to the intended use. In the examples above the different uses would clearly require different levels of QA scrutiny depending on the effect of the data quality on the weight of contribution to the final TMDL decision making. Historical data can be used to determine the expected concentrations of analytes to aid in sampling plan design. Without requiring the rigorous scrutiny of the QA used in collection, the secondary data may serve to provide weight-of-evidence supporting conclusions reached primarily by new data.

In the last two examples, however, where the secondary data will be used in lieu of new data collection, the past data's quality controls should be subject to the same QA controls as new data collection. Secondary data that will substitute for new data or that have a significant effect on the outcome of the TMDL analysis must be assessed to ensure that the data were collected with QA oversight appropriate to the TMDL process, that acceptable methods were used by trained samplers, that samples were analyzed in proper hold times using accurate methods. If possible, the QAPP attached to secondary data will be evaluated and attempts will be made to determine if the QAPP was followed.

An evaluation of secondary data will include:

- Evaluating secondary data relative to TMDL watershed-specific data quality needs
- Understanding the assumptions that are inherent in the secondary data
- Explicitly describing the limitations of the secondary data
- Documenting how the secondary data are useful to help fulfill the TMDL watershed-specific project objectives
- Determining if the secondary data are available in a format that allows their use and documentation.
- Ongoing studies being conducted by the U.S Geological Survey, Sonoma County Water Agency, City of Santa Rosa, The Laguna Foundation, and others.

## **7.0 DOCUMENTATION AND RECORDS**

### **7.1 Documentation**

All documentation by Regional Water Board staff during the development of the Laguna Watershed TMDLs becomes part of the public record. Documentation, from the design of a monitoring program to decision-making, is important to being able to assess the validity of data. Documentation will be used to:

- Allow a sample to be traced from sampling event or field measurement to final result
- Provide a description of the field and laboratory methods used
- Supply observations that would help to interpret or apply the data
- Allow verification of QA program compliance
- Confirm statements about the uncertainty of the data.

The TMDL watershed manager will retain records showing the data that were discarded and an explanation of the reasons for data exclusions. Explanations may include:

- Data were recorded outside of the dates of interest
- Water temperature data show ambient air spikes before or after retrieval or when dewatered
- Instrument malfunctioned
- Data were collected from an incorrect location
- Data were collected using inappropriate instruments
- Data were outside of acceptable QA specifications
- Dead or dying batteries resulted in unacceptable data.

For each sampling event, the field monitoring team shall provide the TMDL watershed project manager with copies of relevant pages of field logs (including raw data), calibration records, copies of the COC forms for all samples submitted to the analytical laboratory, and copies of shipping forms for samples shipped to analytical laboratories. In addition to these documents, the TMDL watershed project manager also will retain laboratory reports and documentation of secondary or historic data/information that is used in TMDL decision-making. The retention and final disposition of the TMDL development records will be in accordance with NCRWQCB protocols (some of the records may be required as part of a regulatory administrative record).

#### **7.1.1 Field Records**

The field monitoring teams will maintain notes in either a bound field notebook or in standardized field record sheets that are prepared for that purpose. A sample field record sheet is found in the SWAMP QAPP. Field crews should use waterproof pen for field notebook; pencils should not be used. The field log/record sheets should document all pertinent field-related information and observations for a sampling episode. The information can help understand the outcome of a sample result and to evaluate the validity of decisions drawn from the data. Such information may include:

- Name of collector
- Sample location
- Sample date and time
- Description of samples collected
- Description and results of field measurements
- Water appearance and odor (e.g., color, unusual amount of suspended matter)
- Weather or recent meteorological events such as rain
- Biological activity (e.g., excessive algal growth, fish presence)
- Watershed or instream activities (e.g., water diversions, mining in the stream, construction, dredging, livestock in stream)
- Pertinent information related to unusual conditions or to water quality, or stream uses
- Specific sampling information (e.g., left bank or right bank sampling, upstream or downstream of notable feature such as a bridge, notes about changes to sampling location, GPS coordinates)
- Missing parameters and an explanation if a parameter could not be sampled
- Observations related to sample transport or miscellaneous problems

### **7.1.2 Corrections to Documentation**

Documents should be corrected only in a manner that allows the reader to view the original, uncorrected data. A single, penned line through the incorrect data should be used. The data and the corrector's initials should be supplied in pen next to the correction. All corrections must be done in ink. A statement explaining the correction may be included in the documentation retained for the project.

## **8.0 REFERENCES CITED**

California Water Resources Control Board. 2002. Quality Assurance Management Plan for the State of California's Surface Water Ambient Monitoring Program. Version 1. Sacramento, California. December 22, 2002.

U.S. Environmental Protection Agency. 2002. Guidance for Quality Assurance Plans. EPA QA/G-5. Office of Environmental Information, Washington, D.C. December 2002.

## **9.0 ACRONYMS**

ADV.....	Acoustic doppler velocimeter
BOD .....	Biochemical oxygen demand
COC .....	Chain of custody
CV .....	Coefficient of variation
DO.....	Dissolved oxygen
DQO.....	Data quality objectives
EPA .....	U.S. Environmental Protection Agency
MQO .....	Measurement quality objective
NCRWQCB ...	North Coast Regional Water Quality Control Board
pH.....	Logarithm of hydrogen ion concentration
QA.....	Quality assurance
QAPP .....	Quality assurance project plan
QC.....	Quality control
SWAMP .....	Surface water ambient monitoring program
TMDL .....	Total maximum daily load
YSI.....	Yellow Springs Instrument